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**(54) Printing plate and method of preparation**

(57) A method of preparing a printing plate comprises producing an oleophilic image on the surface of a support by ink-jet printing the image on the surface using an aqueous solution or aqueous colloidal dispersion of a salt of a hydrophobic organic acid.

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**Description****Field of the Invention**

5 The invention relates to a printing plate and a method of preparing the plate.

**Background of the Invention**

10 Printing plates suitable for offset lithographic printing are known which comprise a support having a surface having non-image areas which are hydrophilic and image areas which are hydrophobic and ink-receptive.

The art of lithographic printing is based upon the immiscibility of oil and water, wherein the oily material or ink is preferentially retained by the image area and the water or fountain solution is preferentially retained by the non-image area. When a suitably prepared surface is moistened with water and an ink is then applied, the background or non-image area retains the water and repels the ink while the image area accepts the ink and repels the water. The ink on the image area is then transferred to the surface of a material upon which the image is to be reproduced; such as paper, cloth and the like. Commonly the ink is transferred to an intermediate material called the blanket which in turn transfers the ink to the surface of the material upon which the image is to be reproduced.

Ink-jet printing is a non-impact method for producing images by the deposition of ink droplets on a substrate in response to digital signals.

20 JP-A-53015905 describes the preparation of a printing plate by ink-jetting an alcohol-soluble resin in an organic solvent onto an aluminium plate.

JP-A-56105960 describes the formation of a printing plate by ink-jetting onto a support e.g. an anodised aluminium plate an ink capable of forming an oleophilic image and containing a hardening substance such as epoxy-soybean oil together with benzoyl peroxide, or a photo-hardening substance such as an unsaturated polyester.

**Problem to be solved by the Invention**

A method of preparing printing plates using the ink-jetting technique is required which avoids the use of organic solvents and/or light-sensitive materials.

**Summary of the Invention**

30 The invention provides a method of preparing a printing plate comprising producing an oleophilic image on the surface of a support by ink-jet printing the image on the surface using an aqueous solution or aqueous colloidal dispersion of a salt of a hydrophobic organic acid.

**Advantageous Effect of the Invention**

40 The method of the invention offers a rapid, simple and direct way to make a printing plate from digital data, using relatively low cost equipment and without light-sensitive materials.

Compared with the ways of preparing a printing plate disclosed in the prior art, the method of the invention requires no processing of the plate and uses dilute aqueous solutions having a low level of environmental impact and low health risk.

**Detailed Description of the Invention**

45 The image on the surface of the printing plate is produced using an aqueous solution or aqueous colloidal dispersion of a salt of a hydrophobic organic acid. Hydrophobic organic acids include a carboxylic, sulphuric or sulphonic acid which bears a substituted or unsubstituted hydrocarbon group which is hydrophobic. The term hydrophobic group is widely understood in the science of surface chemistry. The hydrophobic hydrocarbon group may be aliphatic and/or aromatic, and may be saturated or unsaturated. It may bear substituents e.g. ester, ether or substituted amide groups provided the substituents do not destroy its hydrophobic nature.

50 The hydrophobic organic acid may be a carboxylic, sulphuric or sulphonic acid having at least ten and preferably more than fifteen carbon atoms. It may be used in the form of an alkali metal or ammonium salt. The alkali metal is preferably sodium or potassium, and the ammonium ion is preferably quaternised, for example a tetraalkyl ammonium ion such as tetramethyl or tetrabutyl ammonium.

Suitable hydrophobic organic acids or salts include aliphatic acids such as stearic and palmitic acids, unsaturated aliphatic acids such as oleic and linoleic acid, and surfactants such as sodium bis(tridecyl) sulphosuccinate and petro-

leum sulphonates such as "Petronate L" (trademark of Witco Ltd). Other hydrophobic acids include lauric, myristic, docosanoic and erucic acids.

It is necessary that the salt of the hydrophobic organic acid is in the form of an aqueous solution or a stable colloidal dispersion, so that it can pass through the jets of the printer head.

The salt of the hydrophobic organic acid may be present in the aqueous composition in an amount from 0.005 to 5, preferably from 0.02 to 1 % by weight.

While water is the preferred aqueous carrier medium, the aqueous composition may comprise one or more water miscible solvents e.g. a polyhydric alcohol such as ethylene glycol, diethylene glycol, triethylene glycol or trimethylol propane. The amount of aqueous carrier medium in the aqueous composition may be in the range from 30 to 99.995, preferably from 50 to 95 % by weight.

Jet velocity, separation length of the droplets, drop size and stream stability are greatly affected by the surface tension and the viscosity of the aqueous composition. Ink-jet inks suitable for use with ink-jet printing systems may have a surface tension in the range from 20 to 60, preferably from 30 to 50 dynes/cm. Control of surface tensions in aqueous inks may be accomplished by additions of small amounts of surfactants. The level of surfactants to be used can be determined through simple trial and error experiments. Anionic and nonionic surfactants may be selected from those disclosed in U.S. Patents 5,324,349; 4,156,616 and 5,279,654 as well as many other surfactants known in the ink-jet art. Commercial surfactants include the Surfynol™ range from Air Products; the Zonyl™ range from DuPont; the Fluorad™ range from 3M and the Aerosol™ range from Cyanamid.

The viscosity of the ink is preferably no greater than 20 centipoise e.g. from 1 to 10, preferably from 1 to 5 centipoise at room temperature.

The ink may comprise other ingredients. A humectant or co-solvent may be included to help prevent the ink from drying out or crusting in the orifices of the print head. A penetrant may also be optionally added to help the ink penetrate the surface of the support. A biocide, such as Proxel™ GXL from Zeneca Colours may be added to prevent unwanted microbial growth which may occur in the ink over time. Additional additives which may be optionally present in the ink include thickeners, pH adjusters, buffers, conductivity enhancing agents, anti-kogation agents, drying agents and defoamers.

The aqueous composition is employed in ink-jet printing wherein drops of the composition are applied in a controlled fashion to the surface of the support by ejecting droplets from a plurality of nozzles or orifices in a print head of an ink-jet printer.

Commercially available ink-jet printers use several different schemes to control the deposition of the ink droplets. Such schemes are generally of two types: continuous stream and drop-on-demand.

In drop-on-demand systems, a droplet of ink is ejected from an orifice directly to a position on the ink receptive layer by pressure created by, for example, a piezoelectric device, an acoustic device, or a thermal process controlled in accordance with digital signals. An ink droplet is not generated and ejected through the orifices of the print head unless it is needed. Ink-jet printing methods and related printers are commercially available and need not be described in detail.

The aqueous composition may have properties compatible with a wide range of ejecting conditions, e.g. driving voltages and pulse widths for thermal ink-jet printers, driving frequencies of the piezoelectric element for either a drop-on-demand device or a continuous device, and the shape and size of the nozzle.

The support may be any support suitable for printing plates. Typical supports include metallic and polymeric sheets or foils.

Preferably, a support having a metallic surface is used. Preferably, the metallic surface is oxidised.

In a particularly preferred embodiment of the invention, a support having an anodised aluminium surface is employed.

The support for the lithographic printing plate is typically formed of aluminium which has been grained, for example by electrochemical graining, and then anodized, for example, by means of anodizing techniques employing sulfuric acid and/or phosphoric acid. Methods of both graining and anodizing are very well known in the art and need not be further described herein.

After writing the image to the printing plate, the printing plate may be inked with printing ink in the normal way, and the plate used on a printing press. Before inking, the plate may be treated with an aqueous solution of natural gum, such as gum acacia, or of a synthetic gum such as carboxymethyl cellulose, as is well known in the art of printing - see for example Chapter 10 of "The Lithographer's Manual", edited by Charles Shapiro and published by The Graphic Arts Technical Foundation, Inc., Pittsburgh, Pennsylvania (1966).

The invention is further illustrated by way of example as follows.

#### Example 1

1.08 g of oleic acid was added to 50 g of water containing 1.0 ml of 4M sodium hydroxide, and the solution stirred

until the oleic acid had dissolved. A further 150 g of water was then added. The solution was loaded into the ink cartridge of a Hewlett Packard Deskjet™ 850C ink-jet printer, the cartridge having previously been emptied and cleaned.

An alphanumeric text image was written onto a sheet of Kodak™ PMTII anodised aluminium printing plate material which had been loaded into the printer. The plate was removed and wetted with a 1% w/w aqueous solution of gum acacia, and gently rubbed with a cotton pad wetted with the same solution to which had been applied a little lithographic printing ink ("Rotaprint RF86 Pantone Reflex Blue"). The text image became visible as the ink adhered preferentially to it.

The plate was mounted on a Heidelberg "T-Offset" lithographic printing press using Fishburn "Minilith Black DP3736" printing ink. 1000 sheets of paper were printed with the alphanumeric text image without deterioration of the plate.

## Example 2

A printing plate was prepared and inked as in Example 1, except the "ink" in the ink-jet printer comprised a solution of the tetrabutylammonium salt of oleic acid prepared by mixing 1.0 g of oleic acid in 100 g of water with 9 g of 10% w/w tetrabutylammonium hydroxide solution in 90 g of water.

The plate was mounted on the press and printed as before, and gave 3500 prints of an image comprising alphanumeric text together with a pictorial image rendered in the random halftone pattern delivered by the ink-jet printer. No sign of degradation of the plate was seen after the 3500 prints.

## EXAMPLE 3

Plates were written to and inked by hand with printing ink as in Example 1, using the following aqueous compositions A-E in the ink-jet printer:

A:	
Oleic concentrate	10 g
Water	28 g
Trimethylol propane	2 g

The concentrate was made by adding 1.0 g of oleic acid and 1.0 ml of 4M sodium hydroxide to 194 g of water. When the oleic acid was fully dissolved, 4 ml of a 2% w/w aqueous solution of the dye Acid Blue 92 was added. Trimethylol propane was added as a humectant and the dye was added to assist in making the ink-jet image more visible.

The resulting aqueous solution was 0.125% in oleic acid.

B:	
Stearic acid	0.05 g
25% w/w tetramethylammonium hydroxide	0.3 ml
Water	40 g

C:	
Palmitic acid	0.05 g
25% w/w tetramethylammonium hydroxide	0.3 ml
Water	40 g

D:	
Petronate™ L	0.1 g
Water	38.2 g
Trimethylol propane	2 g
(Petronate™ L is the sodium salt of sulphonated petroleum oil, marketed by Witco)	

E:	
Aerosol™ TR70	0.25 g
Water	50 g
Trimethylol propane	2 g
(Aerosol™ TR70 is a solution of sodium bis(tridecyl) sulphosuccinate, marketed by Cyanamid).	

In every case, printing ink adhered preferentially to the image of the alphanumeric text, showing that a plate capable of offset-litho printing had been formed.

#### Claims

1. A method of preparing a printing plate comprising producing an oleophilic image on the surface of a support by ink-jet printing the image on the surface using an aqueous solution or aqueous colloidal dispersion of a salt of a hydrophobic organic acid.
2. A method according to claim 1 wherein the hydrophobic organic acid is a carboxylic, sulphuric or sulphonic acid having at least 10 carbon atoms.
3. A method according to claim 2 wherein the acid has more than 15 carbon atoms.
4. A method according to any one of the preceding claims wherein the salt is an alkali metal or ammonium salt.
5. A method according to claim 4 wherein the alkali metal is sodium or potassium and the ammonium ion is quaternised.
6. A method according to any one of the preceding claims wherein the salt is an oleate, stearate, palmitate or a petroleum sulphonate.
7. A method according to any one of the preceding claims wherein the salt of the hydrophobic organic acid is present in the aqueous solution or aqueous colloidal dispersion in an amount from 0.005 to 5 % by weight.
8. A method according to any one of the preceding claims wherein the amount of water in the aqueous solution or aqueous colloidal dispersion is from 30 to 99.995 % by weight.

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9. A method according to any one of the preceding claims wherein the surface of the support is a metallic surface.

10. A method according to any one of the preceding claims wherein the metallic surface is an aluminium surface.

5 11. A method according to claim 10 wherein the metallic surface is oxidised.

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# EUROPEAN SEARCH REPORT

Application Number  
EP 98 20 1774

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	EP 0 101 266 A (MILLIKEN RES CORP) 22 February 1984 * page 50, line 9 - page 51, line 3; table I *	1-11	B41C1/10
X	US 3 574 297 A (BROZER KEITH B) 13 April 1971 * column 3, line 50 - line 54; claims *	1-11	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			B41C
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 26 August 1998	Examiner Rasschaert, A
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			

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